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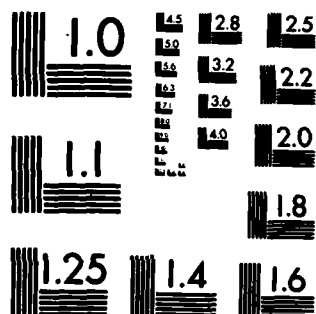
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RESEARCH AND DEVELOPMENT TECHNICAL REPORT

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ELECTROCHEMICAL STUDIES AT CARBON BLACK PASTE
ELECTRODES CONTAINING CUPRIC CHLORIDE ADDITIVE

WISHVENDER K. BEHL
ELECTRONICS TECHNOLOGY & DEVICES LABORATORY

DECEMBER 1982

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additive. Cyclic voltammetry at these microelectrodes also showed that the thionyl chloride reduction peak was also shifted to more positive potentials in the cyclic voltammograms.

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ELECTROCHEMICAL STUDIES AT CARBON BLACK PASTE ELECTRODES CONTAINING CUPRIC CHLORIDE ADDITIVE

INTRODUCTION

Lithium-thionyl chloride cells^{1,2} suffer a loss in performance at high discharge rates (>10 mA/cm²) due to excessive polarization³ of the carbon black cathodes resulting in lower operating voltages as well as lower cell capacities. Since current densities in excess of 10 mA/cm² are required for certain Army applications such as the GLLD laser designator and GVS rangefinder, considerable attention is being given to reduce the excessive cathode polarization and thereby improve the performance of the lithium-thionyl chloride cells at high discharge rates. Thus, various cathode additives (copper,^{4,5} nickel,⁶ platinum,⁷ metal phthalocyanines⁸) have been used to achieve better cathode and cell performance. This report summarizes our results on the use of cupric chloride as a cathode additive for lithium-thionyl chloride cells.

EXPERIMENTAL PROCEDURE

The preparation and purification of thionyl chloride and lithium tetrachloroaluminate have been described in detail elsewhere.⁹ A three electrode system was used for all measurements. The reference and counter electrodes were both made by pressing lithium ribbon onto a nickel screen. The lithium reference electrode was contained in a pyrex tube with a coarse porosity fritted glass bottom. The working electrode (Figure 1) was fabricated by drilling a small cavity (0.24 cm diameter) in one end of an 1/8 inch diameter pyrolytic graphite rod. The latter was then heat sealed in a shrinkable Teflon tubing so that only the cross section of the rod containing the cavity was exposed. The cavity was then filled with the cathode paste and vacuum dried for 16 hours at 120°C.

All cathode pastes contained 10.5 weight percent Teflon binder. Carbon black pastes containing the cupric chloride (21.7 wt %) or copper metal (13.64 wt %) additive were made by adding desired amounts of additive to Shawinigan carbon black before mixing it with Teflon emulsion. Cupric chloride-graphite (80:20 wt %) pastes were similarly made by mixing the constituents in their proper ratio with Teflon emulsion.

The cyclic voltammetric scans were performed with a Tacussel Model PIT-20-2A potentiostat coupled with a Tacussel GSTP-2 function generator and recorded on a Hewlett-Packard Model 7047A x-y recorder. The polarization curves were measured by applying predetermined constant currents (starting from 0.022 mA/cm²) using a precision constant current source (North Hills, Model C-12) for a period of 2 minutes before recording each cathode potential. The potentials were measured by a fluke (Model 8800A) digital multimeter. The discharge curves were recorded on a Hewlett Packard (Model 7100B) strip chart recorder.

RESULTS AND DISCUSSION

Cyclic Voltammograms at Paste Electrodes

Typical cyclic voltammograms obtained, in 1.5 molar LiAlCl₄ - SOCl₂ solutions, at carbon black paste electrodes with and without any additives⁴ are shown in Figure 2. These cyclic voltammograms were found to be similar to those obtained

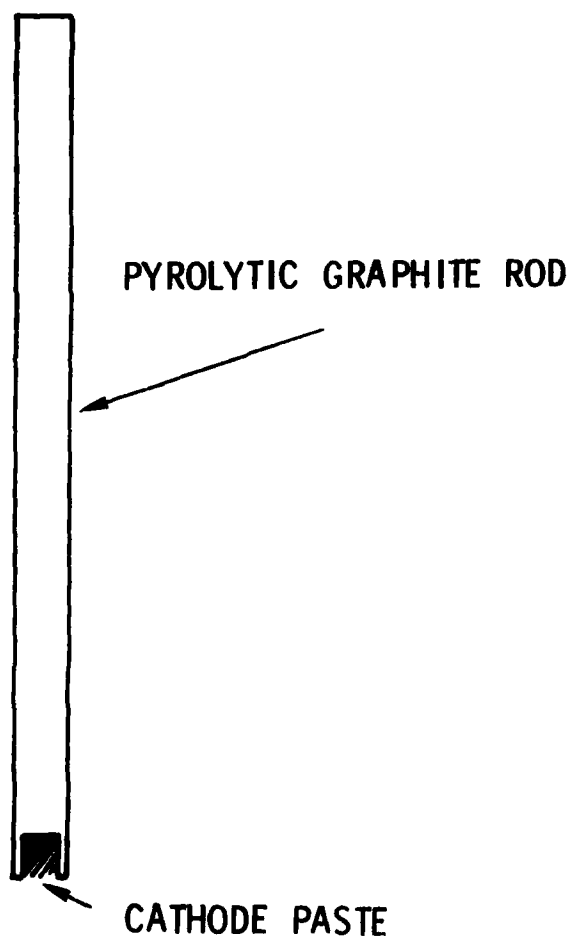


Figure 1. Carbon Black Paste Electrode

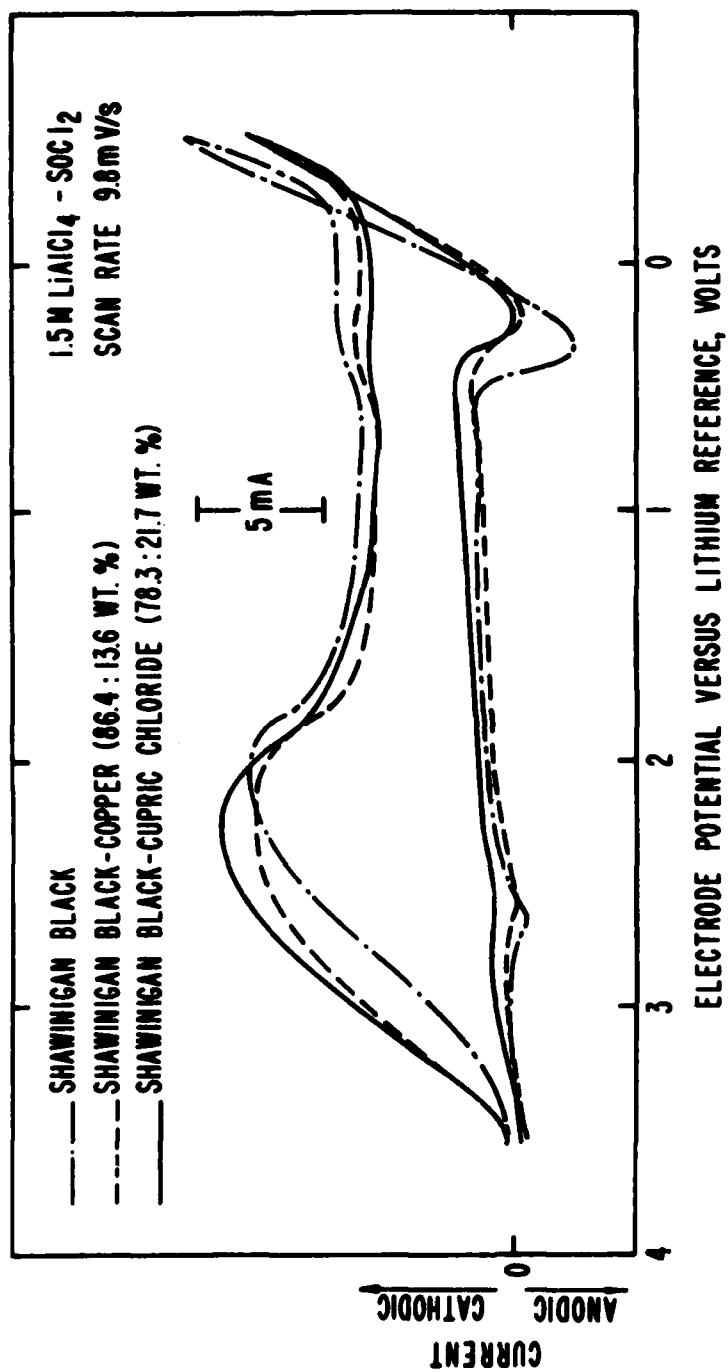


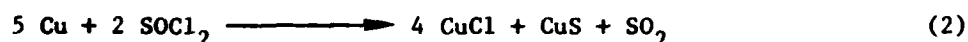
Figure 2. Cyclic Voltammograms at Carbon Black Paste Electrodes in Thionyl Chloride Solutions

at smooth non-porous glassy carbon electrodes.^{10,11} The large reduction peak in the cyclic voltammograms beginning at about 3.5 volts may, therefore, be regarded due to the reduction of thionyl chloride and represented by the equation:

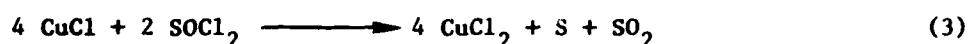


The thionyl chloride reduction peak at the paste electrodes was found to be more drawn out than that observed at glassy carbon electrodes. Further, it was found that the addition of small amounts of cupric chloride to the carbon black paste electrodes resulted in a shift of the large thionyl chloride reduction peak in the cyclic voltammograms (Figure 2) to more positive potentials. A similar effect on the cyclic voltammograms was also observed if the carbon black paste electrodes contained small amounts of copper metal additive.

Copper metal is known¹² to react with thionyl chloride resulting in the formation of mainly cuprous chloride film on the electrode surface

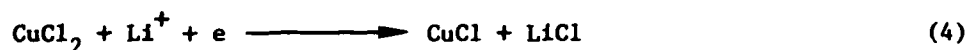


and in $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions, the cuprous chloride film is further oxidized to cupric chloride:

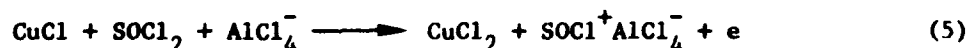


Since copper metal reacts with thionyl chloride in $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions to form cupric chloride, incorporation of copper metal in the cathode structure is equivalent to incorporating cupric chloride assuming that both reactions (2) and (3) proceed to completion. Thus, both copper and cupric chloride additives show similar effects on the cyclic voltammograms.

In a previous study,¹³ we showed that the cupric chloride film formed on copper electrodes in $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions undergoes electrochemical reduction in the solid state to cuprous chloride at ~ 3.5 volts according to the equation:

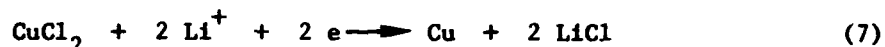


It was also shown that cuprous chloride was oxidized chemically (Equation 3) as well as electrochemically (Equation 5) in $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions to form cupric chloride



Thus, the reduction of cupric chloride film on copper electrodes was found to be reversible and catalytic in $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions. At more negative

potentials (~ 2 volts), cuprous chloride as well as cupric chloride films were both reduced to metallic copper



The reduction of cupric chloride was also examined at paste electrodes in the present study and a typical cyclic voltammogram obtained at cupric chloride-graphite paste electrode is shown in Figure 3. As expected, cupric chloride begins to undergo electrochemical reduction to cuprous chloride (Equation 4) at ~ 3.5 volts resulting in a voltage plateau in the cyclic voltammograms. At more negative potentials, a large reduction peak is observed at ~ 1.6 volts due to the reductions of cuprous and cupric chlorides (Equations 6 and 7) to metallic copper as well as to any simultaneous reduction of thionyl chloride at metallic copper surface (Equation 1). At ~ 0.1 volt, a large increase in cathodic current is observed in the cyclic voltammograms due to the deposition of lithium metal. Except for an anodic peak at ~ 0.4 volts due to the dissolution of the deposited lithium metal, no other anodic peaks were discernible in the cyclic voltammogram on the reverse scan. Thus, the precipitation of lithium chloride in the electrode structure results in passivation of the electrode and also blocks the oxidation of copper metal during the reverse scan.

Galvanostatic Polarization Curves at Paste Electrodes

Polarization curves obtained at Shawinigan carbon black paste electrodes with and without the cupric chloride additive are presented in Figure 4. For purposes of calculating the current densities, cross section area of the cavity (0.045 cm^2) in the pyrolytic graphite rod was used. At small current densities of up to $\sim 2 \text{ mA/cm}^2$, both electrodes show little polarization. However, at higher current densities, the carbon black paste electrode without the cupric chloride additive begins to polarize and polarization gets more severe as the current density is increased. The carbon black paste electrodes containing the cupric chloride additive, on the other hand, show relatively less polarization and exhibit higher cathode voltages at higher current densities than the Shawinigan carbon black paste electrodes without the additive. This is further demonstrated in Figure 5 where Shawinigan carbon black paste electrodes, with and without the cupric chloride additive, were discharged at a current density of 35 mA/cm^2 . Even though the discharge times were approximately equal for both electrodes, Shawinigan carbon black paste electrodes containing the cupric chloride additive exhibited higher cathode voltages than the carbon black cathodes without the additive over most of the discharge span.

The cyclic voltammetric experiments described above indicate that cupric chloride is reduced to cuprous chloride at ~ 3.5 volts, and addition of small amounts of cupric chloride to carbon black paste electrodes results in a shift of the thionyl chloride reduction peak in the cyclic voltammograms to more positive potentials. Similarly, the polarization measurements indicate that the incorporation of cupric chloride in the cathode structure lowers the cathode polarization at high discharge rates. Thus, these studies indicate that cupric chloride is a useful cathode additive for lithium-thionyl chloride cells. The usefulness of the cupric chloride additive may be attributed to the reversible and catalytic nature of the cupric chloride-cuprous chloride redox couple. Thus, the electrochemical reduction of cupric chloride to cuprous chloride (Equation 4)

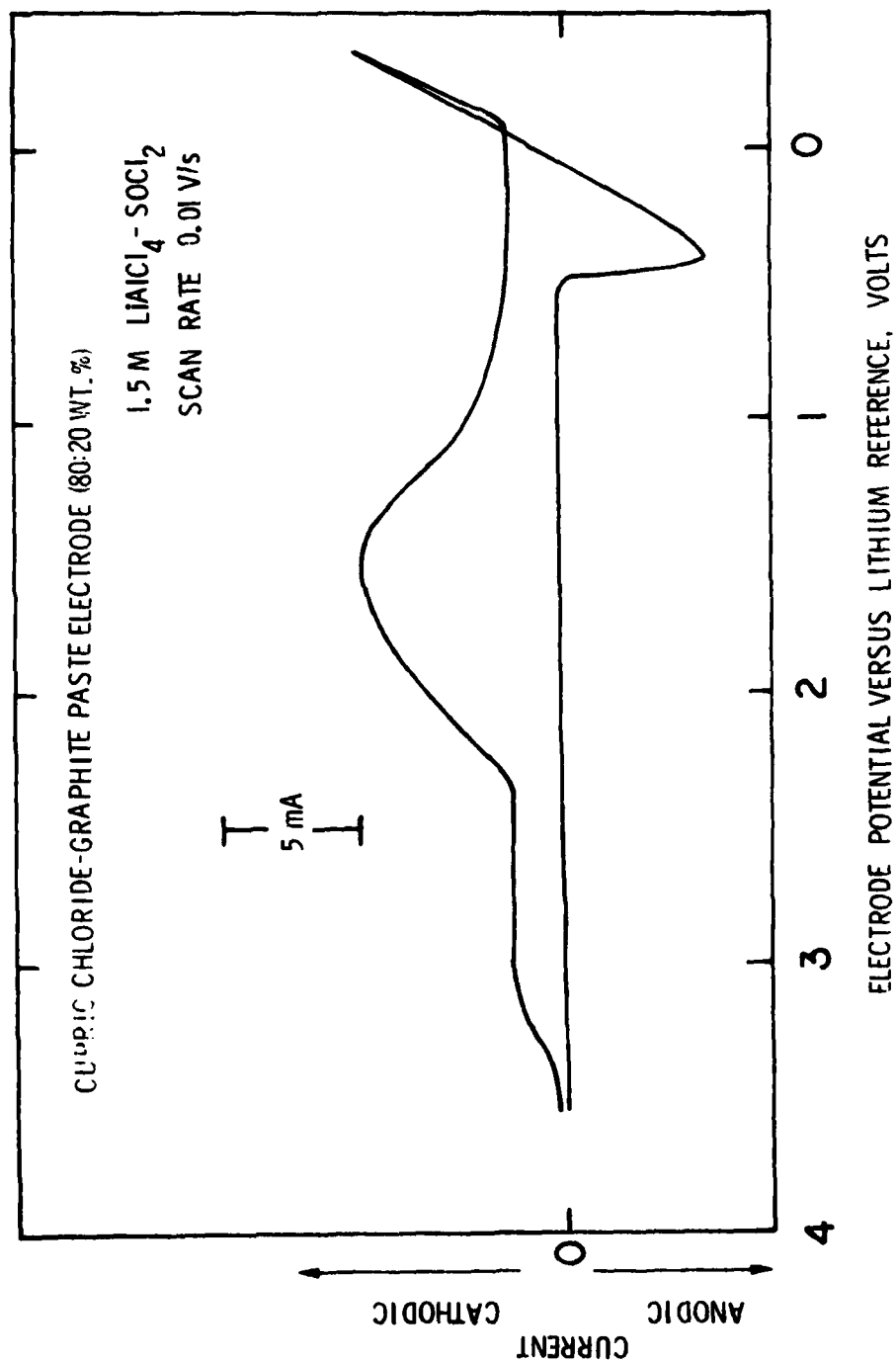


Figure 3. Cyclic Voltammogram at Cupric Chloride-Graphite Paste Electrode

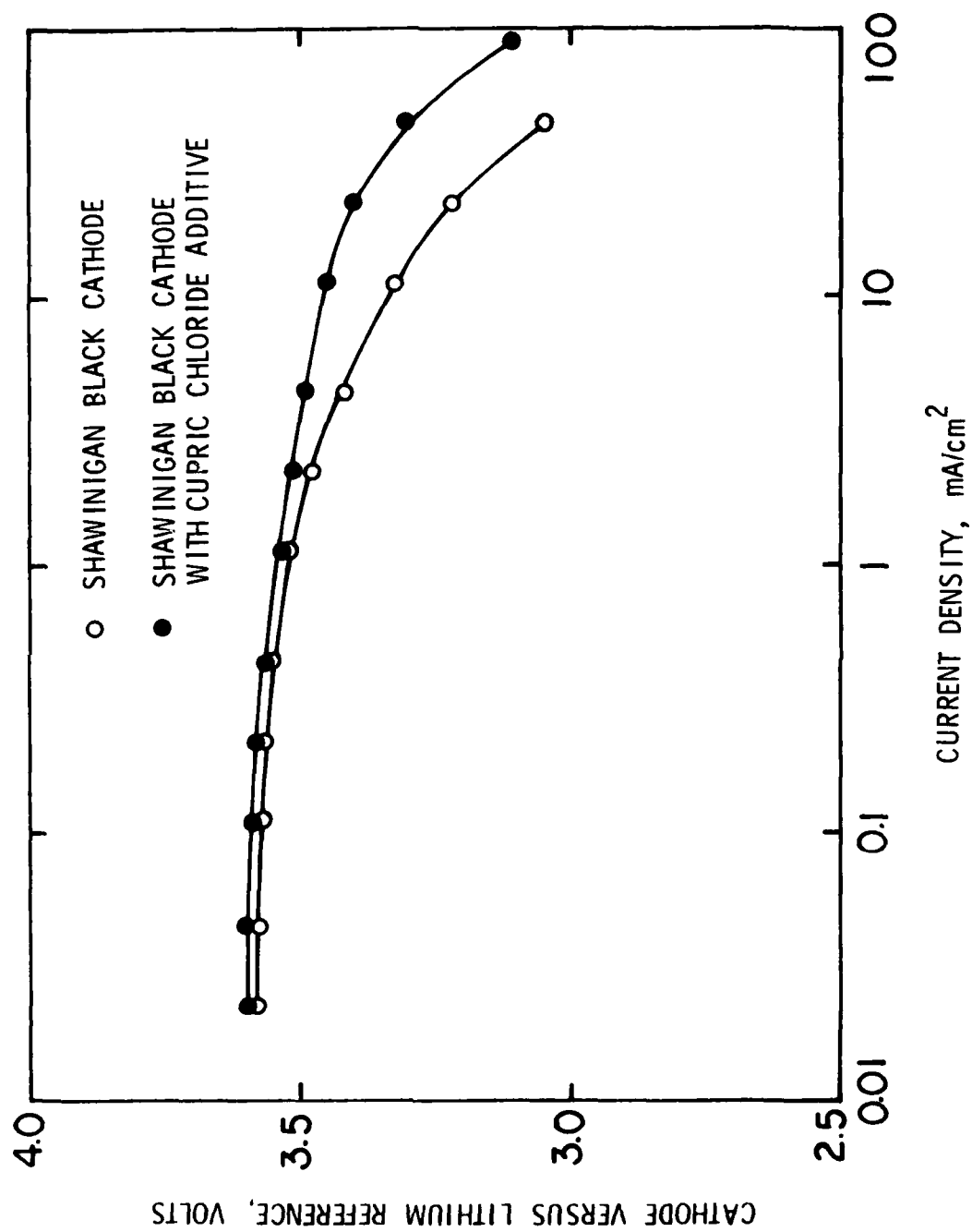


Figure 4. Polarization Curves Obtained at Carbon Black Paste Electrodes in Thionyl Chloride Solutions

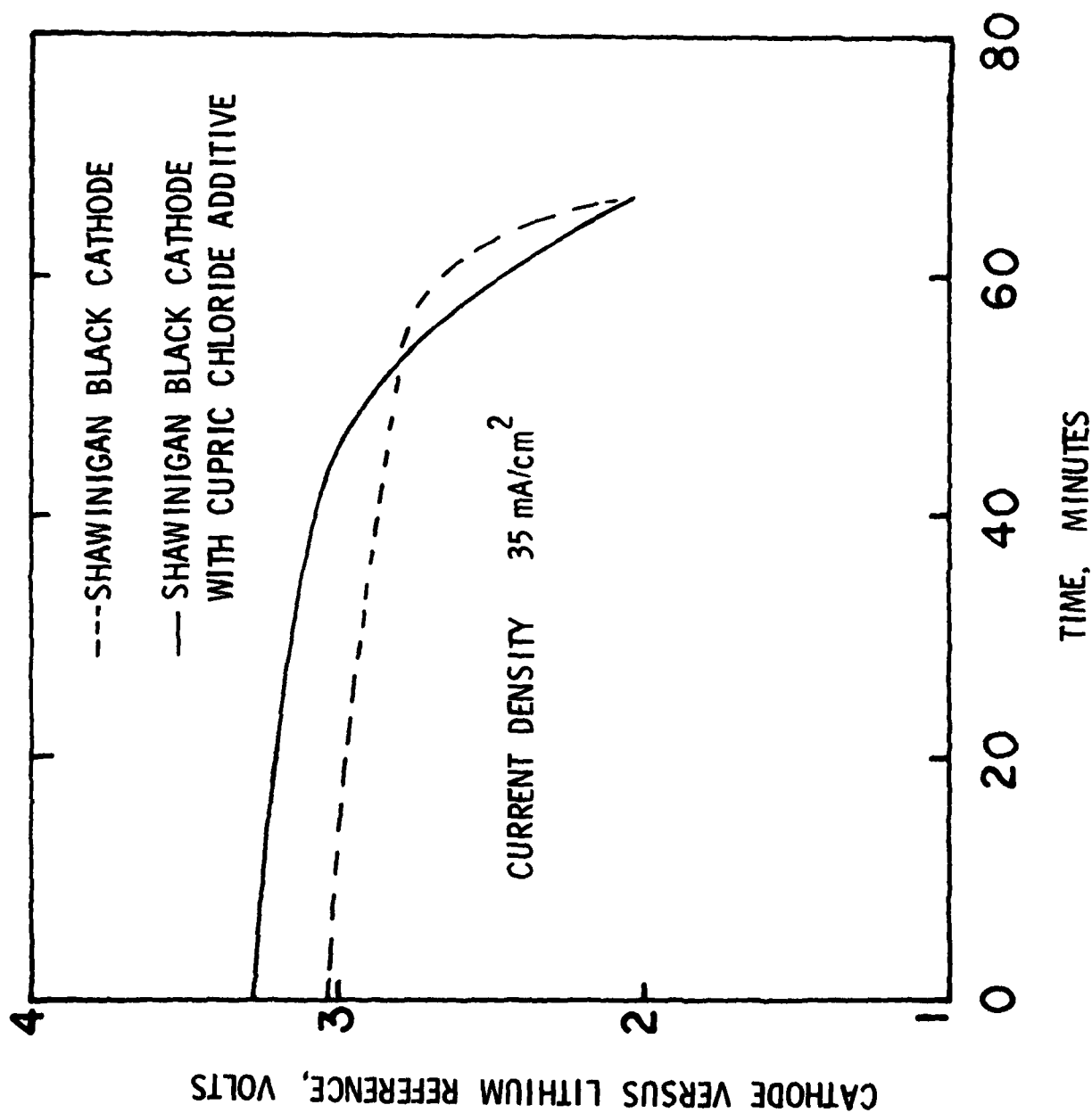


Figure 5. Discharge Curves Obtained at Carbon Black Paste Electrodes in Thionyl Chloride Solutions

in $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions is immediately followed by the chemical reaction between cuprous chloride and thionyl chloride (Equation 3) resulting in the regeneration of cupric chloride. The net result of this electrochemical-chemical reaction is that thionyl chloride is reduced at potentials governed by the cupric chloride-cuprous chloride redox couple. Since the reduction of cupric chloride in $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions is reversible,¹⁴ as opposed to the reduction of thionyl chloride at carbon black electrodes,¹⁵ the cupric chloride-cuprous chloride redox couple shows less polarization than the carbon black electrodes. Thus, the incorporation of cupric chloride in the carbon black structure helps to reduce the excessive polarization of carbon cathodes in lithium-thionyl chloride cells.

CONCLUSIONS

The results of the present study have shown that cupric chloride is a useful cathode additive for lithium-thionyl chloride cells. Thus, Shawinigan carbon black cathodes containing cupric chloride additive exhibited higher cathode voltages under load, particularly at high discharge rates, than the carbon black cathodes without the cupric chloride additive. Copper metal additive was also found to exhibit somewhat similar improvement in cathode performance. However, the use of cupric chloride is preferred since copper metal has to be first oxidized to cupric chloride by $\text{LiAlCl}_4 - \text{SOCl}_2$ solutions in order to become effective as a cathode additive.

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